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(54) **Fuel assembly for nuclear reactor, method for producing the same and structural members for the same.**

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Description

The present invention relates to a fuel assembly for a nuclear reactor, and more particularly to a fuel assembly structural member, made of zirconium (Zr)alloys, such as a fuel cladding tube, a spacer, a channel box or the like.

Structural members of a fuel assembly for a nuclear reactor are generally made of zirconium alloy. Fig. 2 is a schematic cross-sectional view showing a fuel assembly for a BWR (boiling water reactor). The fuel assembly is composed of a number of fuel rods 1 each having fuel pellets in a cladding tube, a spacer 2 for retaining the fuel rods at a predetermined interval, a channel box 3 for encasing the fuel rods and the spacer, an upper tie plate 4 and a lower tie plate 5 for holding upper and lower ends of the fuel rods 1, and a handle 6 for transportation of the assembly as a whole. The fuel cladding tubes 11, the spacer 2 and the channel box 3 of these structural members are made of zirconium alloy and are assembled by welding.

Figs. 3 to 5 show welded portions of the fuel rods 1, the spacer 2 and the channel box 3.

As shown in Fig. 3, end plugs 13 are mounted at welded portions 8 on both ends of each fuel cladding tube 11.

As shown in Figs. 4A to 4D, spacers 2 are classified into two types, i.e., a lattice type and a circular type. The welded portions 8 of the lattice type spacer 2 are joint portions between spacer bars 21 and a spacer band 22, lattice points 23 at each of which the spacer bars 21 intersect with each other, and an overlapped portion of the spacer band 22, as shown in Figs. 4a and 4B. On the other hand, the welded portions 8 of the circular spacer are contact points of spacer rings 25, contact portions between the spacer rings 25 and a spacer band 22, and an overlapped portion of the spacer band 22, as shown in Figs. 4C and 4D.

Fig. 5 shows a shape and welded portions 8 of the channel box 3. The channel box 3 is manufactured by coupling and welding two U-shaped, bent members 31 together, so that two weld lines 8 extends longitudinally.

As described above, any one of the structural members has the welded portions.

The zirconium alloy members are used in the reactor water that is held at a high temperature and a high pressure. In general, the zirconium alloy has a high anti-corrosion and a small neutron absorption cross section. These property of the zirconium alloy is suitable for a fuel assembly structural members for a nuclear reactor. The well known alloy is as follows: zircaloy-2 (Sn: 1.2 to 1.7%, Fe: 0.7 to 0.2%, Cr: 0.05 to 0.15%, Ni: 0.03 to 0.08, Zr: remainder); zircaloy-4 (Sn: 1.2 to 1.7%, Fe: 0.18 to 0.24%, Cr: 0.05 to 0.15%, Zr: remainder); Zr-1,0% Nb alloy; Zr-2.5% Nb alloy; Zr-3.5% Sn-0.8% Nb-0.8% Mo alloy (Excel alloy); Zr-1.0% Sn-1.0% Nb-0.2 to 0.5% Fe alloy; Zr-Nb (0.5 to 5%) Sn-(0 to 3.0%)-any one (up to 2.0%) of Fe, Ni, Cr, Ta, Pd, Mo and W; and the like.

It should be noted that, in the description, % by weight is represented simply by % except for the case where it is necessary to distinguish these expressions.

When the so-called zircaloy, i.e., Zr-Sn-Fe-Cr-(Ni) alloy is used in a boiling water nuclear reactor, there occurs a local oxidation (hereinafter referred to as nodular corrosion). The generation of the nodular corrosion causes a thickness of normal portions of the structural member to be decreased, and at the same time, causes hydrogen generated in accordance with the corrosion reaction to be absorbed into the members, resulting in embrittlement of the members. Since the corrosion phenomenon is developed in accordance with a lapse of time, it is considered that the corrosion of the members is a factor for determining a service life of the fuel assembly under the operational condition of high degree of burn-up in which these members are used for a long period of time. Also, the hydrogen absorption of this alloy is higher than that of Zr-2.5% Nb alloy. Japanese Patent Unexamined Publication No. 58-22364 shows a heat treatment for quenching members from a temperature of $\alpha + \beta$ phase or β phase in order to prevent the nodular corrosion. However, even with this method, it is impossible to prevent the nodular corrosion.

In a Zr-Nb alloy containing Nb, if the amount of Nb is increased, the mechanical strength is increased so that the hydrogen absorptivity is lower than that of the zircaloy. In addition, the local corrosion called "nodular corrosion" does not occur. However, as shown in "proceedings of the International Symposium on Environmental Degradation of Materials in Nuclear Power Systems Water Reactors", Myrtle Beach, South Carolina, August 22-25, pp274-294, since the corrosion resistance property in the weld zone and heat-affected zone thereof is low, there is a problem in using the alloy for the welding structural members. Also, a ductility of the alloy is low so that the alloy is inferior in deformability against impact loads and the like.

Japanese Patent Unexamined Publication No. 61-170552 shows a method for producing a plate member and a tubular member made of high corrosion resistance Zr alloy containing Nb of 0.5 to 2.0%, Sn of 1.5% or less and Fe of 0.25% or less. In order to assemble this alloy as a fuel structural member, it is necessary to weld the high corrosion resistance plate and tubular members, so that the corrosion resistance

property of the weld zone will be again degraded.

USP 3,121,034 shows a method for improving the weldability under the condition that a cold rolling reduction is 50 to 60% and the final heat treatment is performed at a temperature of 550 to 600 °C for 1 to 240 hours, by using Zr-0.5 to 5% Nb alloy, Zr-0.5 to 5% Nb-0 to 3% Sn alloy or quarternary alloy of Zr-0.5 to 5% Nb-0 to 3 Sn-0 to 2% any one of Fe, Ni, Cr, Ta, Pd, Mo and W. However, it would be difficult to perform an intensive working of several tens of percents for the weld structural member.

Japanese Patent Unexamined Publication 47-28594 shows a method for improving anti-corrosion property by annealing Zr-Nb alloy member after welding. However, according to the disclosure of the foregoing literature, even if such a heat treatment is performed, the anti-corrosion property of the welded portions is not improved.

On the other hand, with respect to the fuel structural member of multi-layers, Japanese Patent Unexamined Publication Nos. 54-45495, 54-59660, 55-164396, 56-76088, 58-195485, 58-199836 and 58-216988 show a method in which a Zr liner layer is provided on an inner surface of a tube to thereby preventing a stress corrosion cracking due to a mutual effect between uranium dioxide and plutonium oxide pellets and the inner surface of the tube. However, this method has no effect for improving the corrosion resistance property of the outer surface of the tube.

In the foregoing prior art techniques, there is no total consideration for properties needed in the structural members for fuel of high degree of burn-up, such as a corrosion resistance property of weld zone, a corrosion resistance property of non-welded portions, a tensile property, and resistivity against hydrogen embrittlement. These properties have been incompatible with each other.

SUMMARY OF THE INVENTION

Accordingly, an object of the invention is to provide a fuel assembly for a nuclear reactor, having structural members that are provided with sufficient properties needed in structural members for fuel of high degree of burn-up, such as a corrosion resistance property of weld zone, a corrosion resistance property of non-welded portions, a tensile property and resistance against hydrogen embrittlement. Also, another object of the invention is to provide a method for producing such a fuel assembly and members therefor.

These objects are attained by a fuel assembly as claimed in claim 1.

Dependent claims are directed on features of preferred embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

Figs. 1A to 1C show a basic structure of a fuel assembly for a nuclear reactor according to the invention;

Fig. 2 is a schematic cross-sectional view showing a BWR fuel assembly;

Fig. 3 is a view showing welded portions of a fuel rod;

Figs. 4a to 4d are views showing welded portions of a spacer;

Fig. 5 is a view showing welded portions of a channel box;

Fig. 6 is a chart showing one example of a process for producing a fuel structural member according to the invention;

Fig. 7 is a graph showing an experimental result of the fuel cradding tube in the steam; and

Fig. 8 is a graph showing an experimental result of the spacer in the steam.

DETAILED DESCRIPTION OF THE INVENTION

A fuel structural member according to the invention will now be described with reference to Fig. 1.

In a fuel cladding tube 11, an outer layer 16 in contact with reactor water is made of high corrosion resistance and high strength alloy, an inner surface layer 14 in contact with fuel pellet 21 is made of pure zirconium, and an intermediate layer 15 is made of alloy having a relatively high ductility, as shown in Fig. 1A, thereby performing the objects of the invention.

In a spacer 2 and a channel box 3, a surface layers 26 in contact with the reactor water are made of high strength and high corrosion resistance alloy, and an intermediate layer 27 interposed between the surface layers is made of alloy having a high ductility to thereby perform the above-described objects, as shown in Figs. 1B and 1C.

It is most preferable to use, as the high strength and high corrosion resistance alloy, a Zr-based alloy containing 0.5 to 2.2% Nb-0.5 to 1.5% Sn-0.1 to 0.8% Mo. Also, it is preferable to use, as the high ductility alloy, a Zr-based alloy containing 0.5 to 2.0% Sn-0.05 to 0.4% Fe-0.05 to 0.15% Cr-0.03 to 0.2% Ni, a Zr-

based alloy containing 0.5 to 2.0% Sn-0.05 to 0.4% Fe-0.03 to 0.2% Ni, a Zr-based alloy containing 0.05 to 2.0% Sn-0.05 to 0.4% Fe-0.05 to 0.15% Cr-0.03 to 0.2% Ni-0.01 to 0.8% Mo, stainless steel or copper alloy.

If a Zr-based alloy containing Nb-Sn-Mo and having preferably a tensile strength of 70 kgf/mm^2 or more at room temperature is used in a surface in contact with the reactor water, it is possible to prevent the nodular corrosion and to increase the strength of the member. Furthermore, the degree of the hydrogen absorption of these alloys is small at about 1/5 of that of zircaloy-2 and zircaloy-4. It is thus possible to prevent the hydrogen embrittlement.

If a high ductility alloy preferably with tensile strength of 45 to 60 kgf/mm^2 at room temperature and with an elongation rate 25% or more is used as an intermediate layer interposed between the above-described high strength high corrosion resistance alloy which intermediate layer is out of contact with the fuel pellet, or as an intermediate layer interposed between a pure Zr liner layer, which preferably has a tensile strength of 30 to 40 kgf/mm^2 and an elongation rate 30% or more, and the high strength high corrosion resistance alloy, the ductility of the member is enhanced, and in particular, the toughness of a member such as a spacer that is subjected to a impact load during the fuel handling is enhanced. The elongation rate is preferable 30% or more.

As a material forming the intermediate layer, other than those described above, it is preferable to use copper alloy and stainless steel. The tensile strength of these materials at room temperature is shown in Table 1.

Table 1

material		Composition (%)	tensile strength (kgf/mm^2)	elongation (%)
copper alloy	8% Al bronze	8.0Aℓ-92.0Cu	45.7	60
	berylium copper	2.0Be-98.0Cu	48.5	35
	nickel copper	66.0Ni-34.0Cu	53.9	42
AISI	304	-	53.0	40
	304L	-	49.0	40
	347	-	53.0	40
	316	-	53.0	40
	316L	-	49.0	40

Since the high strength high anti-corrosion alloy contains Nb, it is necessary to prevent the reduction in anti-corrosion property of welded portions. In order to satisfy this requirement, the alloy composition must meet the following relationship:

[Sn addition amount] (wt%) ≧
2 x [Nb addition amount] (wt%) -3.0

In addition, the alloy should be heat-treated in the temperature range of 500 to 700 °C after welding. In particular, it is preferable to effect the heat treatment for heating the alloy for 1 to 30 hours in the temperature range of 530 to 610 °C.

The reasons therefor will be described below. The causes for the degradation in corrosion resistance property of the weld zone and the heat-affected zone thereof are that a non-equilibrium phase in which a great amount of Nb exists in a solid-solution state is formed during a heating/cooling process in welding. The non-equilibrium phase is formed in such a manner that β phase stable at a high temperature is formed in the weld zone and the heat-affected zone thereof and is quenched. The β phase remains at the room temperature, or is not decomposed into an α-Zr phase and a β-Nb precipitated phase stable at room temperature in the cooling process, and the β phase is martensite-transformed into ω Zr phase.

The corrosion resistance property of this phase is extremely low, which causes the reduction in anti-corrosion property in weld zone. The purpose of the heat treatment after welding is to decompose the non-equilibrium phase into the α-Zr phase and the β-Nb precipitated phase stable at room temperature.

Also, the reason why the element of Sn is added to meet the above-described relationship is that Sn has an effect for preventing the generation of the non-equilibrium phase during the cooling process in welding and an effect for accelerating the decomposition of the non-equilibrium phase still remaining after welding.

The reason why the upper limit of preferable temperature range is 610 °C is that, if the alloy is heated above the upper limit, the β phase will be again formed and the β Nb phase that is finely precipitated in the α Zr phase to enhance the strength will be diffused into the β phase to thereby remarkably reduce the strength.

The reason why the lower limit of the preferable temperature range is 530 °C is that the worked structure generated by cold working or the like is heated at 530 °C or above so as to be recrystallized for enhancing the ductility of the material and for promoting the decomposition of the non-equilibrium phase remaining in the welded portions.

The heating in the temperature range of 530 to 610 °C is performed for the purposes of preventing the crystalline particle of the high ductility alloy interposed between the high strength high anti-corrosion alloys from becoming coarse and of preventing superior ductility being degraded.

It is preferable that a thickness of the high strength high anti-corrosion alloy be in the range of 5 to 20%. If the thickness is smaller than the lower limit, it would be very difficult to control the thickness during the manufacture. The upper limit thereof depends upon the necessary strength.

More specifically, in a structural member having a thickness of, for example, 860 μm, if the thickness of the innermost layer is less than 50 μm, it is difficult to control the thickness during the manufacture. Also, the maximum value is 150 μm in view of I_2 SCC of the pure zirconium. Therefore, the thickness of the innermost layer is about 5.8 to 17.4% of the total thickness. Preferably, it is 5 to 20% thereof.

On the other hand, from a view point of the anti-corrosion property and the strength, the thickness of the outermost layer is in the range of 100 to 480 μm, that is, in the range of about 11.6 to 55.8% of the total thickness. It is preferable the range of the thickness of the outermost layer be 10 to 60%, and in particular, in case of a cladding tube, it is preferable that the thickness of the outermost layer be 15 to 30%, and as other requisite, it is preferable to make the thickness of a single layer be in the range of 20 to 35%.

In case of the intermediate layer, the maximum and minimum values are varied depending upon the mechanical strength of the material to be used. An example of the maximum and minimum values in case of the intermediate layer of copper alloy or stainless steel is shown in Table 2. It is preferable to set the thickness of the intermediate layer in the range of 25 to 85%. In particular, in case of the cladding tube, it is preferable to set the intermediate layer thickness in the range of 50 to 70%, and in case of other members, it is preferable to set the intermediate layer thickness in the range of 35 to 60%.

Table 2

		Max. (mm) (% regarding the total thickness)	Mini. (mm) (% regarding the total thickness)
copper alloy	8% Al bronze	0.542 (about 63%)	0.23 (about 27%)
	berylium copper	0.580 (about 67%)	" "
	nickel copper	0.70 (about 81%)	" "
AISI	304	0.68 (about 79%)	" "
	304L	0.60 (about 69%)	" "
	347	0.68 (about 79%)	" "
	316	0.68 (about 79%)	" "
	316L	0.60 (about 69%)	" "

The method for producing the above-described fuel structural member of three-layer structure will be described. Interfaces of the three-layer structure are preferably a metallurgically bonded faces.

Fig. 6 is a view showing an example of a process for producing the fuel structural member according to the present invention.

The integration is performed by the mutual diffusion of metal atoms between the materials at the time of hot rolling or hot extruding and intermediate annealing after cold rolling. When a stable phase such as an oxide film is formed on a surface of the material, this phase becomes a barrier against the mutual diffusion, resulting in inferior metallurgical bonding. Accordingly, any work that contaminate the surface must be avoided.

After the surface is cleaned prior to the hot rolling or hot extruding, the materials forming the respective layers are overlapped with each other. At this time, end faces thereof are welded together to prevent air or the like from entering into the interior. When the welding work is performed in the atmosphere, there is a fear that an oxide layer is formed in the interface in welding. Therefore, it is preferable to perform the welding work under vacuum condition.

The higher the hot extruding temperature or hot rolling temperature, the more the mutual diffusion between the materials will be accelerated. Thus, this is preferable for the metallurgical bonding. However, very coarse β phase crystal grains will be caused in the temperature range exceeding 1,100 °C. This is undesirable.

If the materials are heated up to the $\alpha + \beta$ phase temperature or the β phase temperature, the diffusion of alloy elements will be extremely accelerated. This is preferable for the metallurgical bonding.

Accordingly, it is effective to insert after the hot working a step of heating the materials to the $\alpha + \beta$ phase temperature or the β phase temperature and then air- or water-cooling the materials. It is necessary that the water cooling rate be 8 °C/sec or more. If the cooling rate is lower than this limit, the precipitated phase will become coarse, to degrade the mechanical property.

After this heat treatment, the cold rolling and annealing must be performed at least once. Since the ductility of the material cooled from the $\alpha + \beta$ phase or the β phase is low, it is necessary to grow new crystalline perticles having no strain by heating the material above the recrystallization temperature after forming a working structure through the cold rolling. This treatment recovers the ductility.

The invention is explained below in detail by use of embodiments.

〈Embodiment 1〉

Table 3

No.	Kinds of Material	Alloy elements (wt%)							
1	Pure Zr	Sn -	Fe 0.03	Ni -	Cr -	Nb -	O 0.06	Zr 99	Mo -
2	Zircalloy	1.5	0.25	0.09	0.1	-	0.11	bal	-
3	NSM alloy	1.0	-	-	-	1.0	0.09	bal	0.5

Table 4

Material	σu (kg/mm^2)	$\epsilon \ell$ (%)
Pure Zr	35	34
Zircalloy-2	56	34
NSM alloy	80	20

By using a vacuum arc melting method, there were produced a pure Zr ingot, a Zr-Sn-Fe-Ni-Cr alloy ingot, and a Zr-Sn-Nb-Mo alloy ingot. The alloy composition of each of the ingots is shown in Table 3, and the data of strength and elongation about each layer are shown in Table 4.

Each of the ingots was forged at a temperature of 980 to 1050 °C (β forging) and the forged billets were formed into billets having diameters different each other. The forged billets were subjected to a heat-treatment (β quenching) in which the billets were water-cooled after being held at 1000 °C for one hour.

After removing the surface oxide layer occurring on the β-quenched billet materials by mechanical grinding, the billets were subjected to piercing so that the billets were provided with axial holes of diameters different each other. The inner diameter of the hole provided in the Zr-Sn-Fe-Nb-Mo alloy pierced cylindrical billet was approximately equal to the outer diameter of the hole provided in the Zr-Sn-Fe-Ni-Cr alloy pierced cylindrical billet, the latter being inserted in the former by use of a press. The outer diameter of the hole provided in the pure Zr billet was approximately equal to the inner diameter of the pierced Zr-Sn-Fe-Ni-Cr alloy billet, the pure Zr billet being inserted in the latter billet by use of the press so that the three billets were integrated.

The inner diameter of the integrated billets was made to be 50 mm and the outer diameter thereof was made to be 150 mm, in which integrated billets the thickness of the Zr-Sn-Nb-Mo alloy was 10 mm, the thickness of the Zr-Sn-Fe-Ni alloy being 30 mm, and the thickness of the pure Zr being 10 mm. The boundary portions of the ends of the intergrated billets were welded under a high vacuum not less than 1×10^{-4} Torr by an electron beam welding device. Then, the integrated billets were hot-extruded after being heated to 750 °C, with the result that there was produced a tube having an outer diameter of 64 mm and a thickness of 11 mm. Then, the tube was cold-rolled two times by use of pilger mills, so that there was obtained a tube having an outer diameter of 19.2 mm and a thickness of 1.9 mm.

During the production of the tube, an intermediate annealing treatment was effected at 630 °C in 2 hours after the first cold-rolling, then the tube was subjected to a heat-treatment ($\alpha + \beta$ quenching) in which water was jetted onto the tube to effect the cooling thereof just after the tube passed a high frequency induction coil. After the heat-treatment, the tube was again rolled two times by the pilger mills to thereby obtain a tube having an outer diameter of 12.3 mm and a thickness of 0.86 mm, the intermediate annealing being effected at 590 °C in 2 hours, and the final annealing was effected under vacuum at 570 °C for 2 hours.

In the resultant tube there was inserted uranium pellets, and then plugs were attached to both the ends of the tube, which plugs and the tube ends were joined by TIG welding under a He atmosphere of 3 atm, so that a fuel rod was obtained. The weld zones each defined by both the plug and the tube end was heated in

a He atmosphere at 580 °C and held in about 10 minutes, then being cooled.

From both the weld zone and the center portion of the resultant fuel rod there were cut out test pieces, which were subjected to a corrosion test and a tensile test. The corrosion test was effected at a temperature of 500 °C in steam of a pressure of 105 kgf/cm^2 by holding them in 24 hours. Other test pieces were polished and etched to examine the thickness of each layer.

As a result, it was found that the cross-sectional thickness of the pure Zr was 18% of the whole thickness of the fuel cladding tube, that the thickness of the Zr-Sn-Fe-Ni-Cr alloy layer is 62% thereof, and that the thickness of the Zr-Sn-Nb-Mo alloy layer is 20% thereof, that is, the thickness ratio of the layers was in proportion to the thickness ratio of the initial billets forming the integrated billets.

As apparent from Fig. 7 showing the test results under steam, the corrosion resistance of the material of the invention was very high with respect to both the weld zone and the center portion of the fuel cladding tube in comparison with the comparative material. Further, neither nodular corrosion nor accelerated corrosion of white color occurred on the outer surface (Zr-Sn-Nb-Mo alloy layer) of the material of the invention, which outer surface was covered with uniform oxide film of black color.

On the other hand, in the comparative material, there were observed at both the weld zone and the center portion thereof much amount of nodular corrosion with respect to the test under steam. The remarkable difference in corrosion resistance occurring therebetween in the test under steam is attributed to the matter regarding whether or not the nodular corrosion occurred.

In the tensile test, the tensile strength of the material of the invention was 63 kgf/mm^2, the elongation thereof being 38%, so that the tensile strength of the material of the invention is higher by 5 to 8 kgf/mm^2 than a conventional fuel cladding tube made of Zircalloy-2 and the elongation of the material of the invention is in the same degree in comparison therewith.

〈Embodiment 2〉

Table 5

No.	Kinds of Material	Alloy elements (wt%)						
1	Zircalloy	Sn 1.0	Fe 0.3	Ni 0.1	Cr 0.05	Nb -	Mo -	Zr bal
2	NSM	1.0	-	-	-	2.0	0.2	bal

By use of a vacuum melting method, two kinds of alloys shown in Table 5 were melted to thereby provide ingots. The ingots were forged at a temperature of 980 to 1050 °C to provide slabs of 75 mm in thickness. The forged slabs was subjected to β quenching in which the water cooling thereof was effected after holding the slabs at a temperature of 1000 to 1050 °C in 20 minutes. The alloy No. 1 shown in Table 5 was hot-rolled at a temperature of 600 °C to have a thickness of 35 mm, the alloy No. 2 being hot-rolled at a temperature of 750 °C to have a thickness of 20 mm.

After the hot rollings thereof, the surfaces of both the alloys were finished by mechanical grinding. Then, the finished alloy No. 1 was sandwiched between two pieces of plates of the alloy No. 2. The end faces of the three pieces of plates overlapped each other were integrated by electron beam welding, which integrated plates were hot-rolled two times at 780 °C to provide sheet having a thickness of 3 mm, which sheet was further cold-rolled to have a thickness of 2 mm and was subjected to an annealing treatment in which it was held at 650 °C in 2 hours. After that, it was held at 870 °C in 5 minutes and then cooled by jetting water onto both surfaces of the sheet.

The sheet was further cold-rolled three times to provide a strip used for a spacer which strip had a thickness of 0.53 mm. Annealing was effected between adjacent two cold-rollings at 590 °C in 1 hour, while the final annealing was effected at 570 °C in 1 hour. From the strip there was formed a spacer band shown in Fig. 4B by punching, and it was subjected to a dimple working.

Further, from the alloy ingots shown in Table 5 there were produced cylindrical billets. The billet of the alloy No. 1 (the intermediate layer billet) was sandwiched by the outer and inner two billets (the outer and inner surface layer billets) of the alloy No. 2 shown in Table 5, which outer surface layer billet of the alloy No. 2 had an outer diameter of 150 mm and a thickness of 15 mm, which intermediate layer billet had a thickness of 20 mm, and which inner surface layer billet had a thickness of 15 mm.

The production process thereof was the same as the embodiment 1 with the exception of the size as shown above, that is, the end faces defined by those of the billets in a sandwich state was integrated by electron beam welding and then the integrated billets were hot-rolled at 750 °C to provide a tube having an outer diameter of 64 mm and a thickness of 11 mm, which tube was rolled one time by a pilger mill to obtain a tube having an outer diameter of 34.9 mm and a thickness of 4.4 mm. The whole length of the tube was then subjected to a treatment in which it was heated to 870 °C while passing a high frequency induction heating coil portion and water was jetted thereon to quench the tube at the position just under the heating portion. After the treatment, it was heat-treated at 600 °C for 1 hour. Further, the cold working and intermediate annealing were alternately effected three times to obtain a tube having an outer diameter of 14 mm and a thickness of 0.6 mm, the temperature of which intermediate annealing was 590 °C. The tube was cut to obtain tube members each having a length of 25 mm, which members were plastically worked with a plate spring 28 being attached to each of the tube member so that the tube members was formed into a spacer ring 25 of such configuration as a fuel rod was able to be held in each of the tube members. A plurality of spacer rings were assembled to form a rounded cell type spacer lattice of 9x9 pieces, spacer band 22 being disposed around the outer periphery of the lattice and being spot-welded to thereby obtain a rounded type spacer. After the completion of the assembling thereof, the whole was heat-treated by holding it at 530 °C for 10 hours.

From the spacer there were cut out test pieces a part of which included a weld zone, the test pieces being subjected to corrosion test in steam of 500 °C.

After finishing the corrosion tests of both the material of the invention and comparative material (Zircalloy-2), results with respect to the increment of corrosion are shown in Fig. 8. According to the results of the corrosion test in steam, the material of the invention has very high corrosion resistance in comparison with the comparative material. Further, according to appearance observation of the test pieces which observation was effected after the finish of the corrosion test, the surface of the material of the invention was covered with uniform oxide film of black color, and neither nodular corrosion nor accelerated corrosion of white color were observed on the surface thereof.

On the other hand, much nodular corrosion was observed on the comparative material having been subjected to the corrosion test in steam. This remarkable difference therebetween with respect to corrosion resistance evaluated in steam was attributed to whether or not the nodular corrosion occurred.

After the corrosion test, the content of hydrogen contained in the material of the invention was analyzed, so that the hydrogen absorption rate thereof was 3%. Also, a plate material made of the alloy No. 1 alone and another plate material made of the alloy No. 2 alone were subjected to corrosion test in high temperature water, and the hydrogen absorption rates thereof were measured with the results that the hydrogen absorption rate of the alloy No. 1 was 35% while the hydrogen absorption rate of the alloy No. 2 was 3%. Thus, it was found that the hydrogen absorption rate of the structure members of the fuel assembly for nuclear reactor according to the invention is the same level as the alloy No. 2.

Further, a plate of the alloy No. 2 alone provided with a notch was subjected to impact test with the result that the absorption energy thereof was a low value of 3 $kg \cdot m/mm^2$, while the absorption energy of the plate of three-layer structure of the invention was 20 $kg \cdot m/mm^2$ which was a very improved value in comparison with the former.

Thus, by forming the three-layer structure according to the invention, no nodular corrosion occurs, corrosion resistance being improved in a great degree, toughness being improved, and hydrogen absorption rate is lowered.

〈Embodiment 3〉

Slabs of the same alloy compositions as in the Embodiment 2 were formed, being then integrated by electron beam welding, and were formed into a plate having a thickness of 75 mm by use of the same process as in the Embodiment 2, wherein the thickness of each alloy was the same value as in the case of the spacer band shown in the Embodiment 2. The plate was then hot-rolled at 780 °C to have a thickness of 20 mm, the plate being again hot-rolled at 780 °C after having been heat-treated at 650 °C in 2 hours to thereby be formed into a sheet having a thickness of 3 mm. The sheet was cold-rolled into a thickness of 2.6 mm after having been held at 600 °C in 2 hours. The final annealing was effected at 600 °C in 2 hours. This sheet was bent to a channel shape, by use of which sheet there was produced a tube of a square cross section by TIG welding. After the welding, bead portions occurring in the welding were flattened by rolling. Thereafter, a mandrel made of a stainless steel was inserted in the interior of the tube of square cross-section, which tube was then held at 600 °C in 2 hours. During this heat treatment, the square tube was plastically deformed in compliance with the shape of the mandrel because the linear expansion

coefficient of the stainless steel is higher than that of the structural member, so that the square tube was formed to have a predetermined size.

Test pieces were cut out from the weld zone of the channel box thus produced and were subjected to corrosion test, with the result that the same high corrosion resistance as in the Embodiments 1 and 2 was able to be confirmed.

Also, it was confirmed that, by replacing the Zr-Sn-Fe-Ni-Cr alloy in these Embodiments by Zr-Sn-Fe-Ni-Cr-Mo alloy, there were able to obtain results similar to those of these Embodiments.

According to the invention it is possible to prevent nodular corrosion from occurring and to prevent accelerated corrosion from occurring inherently in a weld zone of an alloy containing Nb. Further, in the invention it is also possible to reduce the hydrogen absorption rate into a degree of not more than 1/10 in comparison with that of the conventional Zircalloy shown in Table 5 and at the same time it is possible to enhance toughness against impact load. Thus, in the invention it is possible to greatly prolong the service life period of a fuel construction member disposed in a nuclear reactor, so that there can be obtained a fuel assembly for nuclear reactor and a member thereof both sufficiently compatible with a tendency to make the degree of burn-up of fuel higher.

Claims

1. A structural member for a fuel assembly for nuclear reactor, comprising three-layer structure having:
an inner surface layer, an outer surface layer and an intermediate layer interposed therebetween, the outer surface layer and eventually the inner surface layer is/are in contact with the reactor water of the nuclear reactor,
characterized in that
said outer surface layer and eventually the inner surface layer is/are made of a Zr-based alloy containing Nb, Sn, and Mo, and that said intermediate layer is made of a high ductility alloy which is higher in ductility than the outer surface layer and which is higher in strength than the inner surface layer.

2. A structural member according to claim 1,
characterized in that said member is a fuel cladding tube (11) wherein said inner surface layer (14) is in contact with nuclear fuel (21) which inner surface layer (14) is made of pure zirconium, and an intermediate layer (15) made of a high ductility alloy which is higher in ductility than the outer surface layer (16) and which is higher in strength than the inner surface layer (14).

3. A structural member according to claim 1,
characterized in that
said member is a fuel spacer (2).

4. A structural member according to claim 1,
characterized in that
said member is a fuel channel box (3).

5. A structural member for nuclear reactor of any one of the claims 1 to 4, wherein a Zr-based alloy containing Nb, Sn and Mo, which alloy constitutes the outer surface layer (16; 26; 31), and eventually the inner surface layer consists by weight of 0.5 to 2.2 % Nb, 0.5 to 1.5 % Sn, 0.1 to 0.8 % Mo, and the balance Zr and incidental impurities.

6. A structural member for nuclear reactor of any one of the claims 1 to 5, wherein the high ductility alloy forming the intermediate layer (15; 27) consists of a Zr-based alloy containing Sn, Fe and Ni.

7. A structural member for nuclear reactor of claim 6, wherein the high ductility alloy forming the intermediate layer (15; 27) consists by weight of 0.5 to 2.0 % Sn, 0.05 to 0.4 % Fe, 0.03 to 0.2 % Ni, and the balance Zr and incidental impurities.

8. A structural member for nuclear reactor of any one of the claims 1 to 5, wherein the high ductility alloy forming the intermediate layer (15; 27) is a Zr-based alloy containing Sn, Fe, Ni and Cr.

9. A structural member for nuclear reactor of claim 8, wherein the high ductility alloy forming the intermediate layer (15; 27) consists by weight of 0.5 to 2.0 % Sn, 0.05 to 0.4 % Fe, 0.03 to 0.2 % Ni, 0.05 to 0.15 % Cr, and the balance Zr and incidental impurities.

10. A structural member for nuclear reactor on any one of claims 1 to 5, wherein the high ductility alloy forming the intermediate layer (15; 27) is a Zr-based alloy containing Sn, Fe, Ni, Cr and Mo.

11. A structural member for nuclear reactor of claim 10, wherein the high ductility alloy forming the intermediate layer (15; 27) consists by weight of 0.5 to 2.0 % Sn, 0.05 to 0.4 % Fe, 0.03 to 0.2 % Ni, 0.05 to 0.15 % Cr, 0.01 to 0.8 % Mo, and the balance Zr and incidental impurities.

12. A structural member for nuclear reactor of any one of claims 1 to 5, wherein the high ductility alloy forming the intermediate layer (15; 27) consists by weight of 0.1 to 0.7 % Nb, and the balance Zr and incidental impurities.

13. A structural member for nuclear reactor of any one of claims 1 to 5, wherein the high ductility alloy forming the intermediate layer (15; 27) is a stainless steel consisting by weight of not more than 0.08 % C, not more than 2.0 % Mn, not more than 1.00 % Si, 16.0 to 20.0 % Cr, 8.00 to 14.00 % Ni, not more than 3.00 % Mo, and the balance Fe and incidental impurities.

14. A structural member for nuclear reactor of any one of claims 1 to 5, wherein the high ductility alloy forming the intermediate layer (15; 27) is a Cu-based alloy consisting by weight of not more than 3.0 % Pb, not more than 6.0 % Fe, not more than 0.5 % Zn, not more than 11.0 % Al, not more than 2.0 % Mn, not more than 33.0 % Ni, and the balance Cu and incidental impurities.

15. A structural member for nuclear reactor of any one of claims 2 and 4 to 14, wherein in the fuel cladding tube (11) the thickness of the outer surface layer (16) and eventually the inner surface layer in contact with the reactor water of the nuclear reactor is 10 to 30 % of the total thickness of the cladding tube (11), and in the channel box (3) the thickness of the outer surface layer (31) in contact therewith is 20 to 35 % of the total thickness of the channel box.

16. A method of producing a structural member for a fuel assembly for nuclear reactor, said structural member comprising three-layer structure having:
an inner surface layer, an outer surface layer and an intermediate layer, said outer surface layer and eventually said inner surface layer is/are in contact with reactor water of the nuclear reactor,
characterized in that
said outer surface layer and eventually the inner surface layer is/are made of a Zr-based alloy containing Nb, Sn, and Mo,
said intermediate layer is made of a high ductility alloy which is higher in ductility than the outer surface layer and which is higher in strength than the inner surface layer,
said method comprises the steps of: integrating, by use of thermal bonding, said three-layered structure having said intermediate layer and said inner and outer surface layer subjecting said integrated three-layered structure to a heat-treatment so that said structure is heated and maintained at a temperature of $\alpha + \beta$ phase of said Zr-based alloy or of the β phase of said Zr-based alloy and so that said structure is quenched after the heating; subjecting the heat-treated three-layered structure to cold plastic working and annealing to thereby obtain a thin thickness member; effecting working and welding of the thin thickness member to obtain the structural member having a desired shape; and subjecting the structural member to a heat-treatment at a temperature of 400 to 700 °C.

17. A method according to claim 16,
characterized in that
said member is a tubular or plate-like member and the step of effecting a heat-treatment at a temperature of 400 to 700 °C is carried out after welding the end face of said member.

18. A method according to claim 16 of producing the structural member for nuclear reactor of any one of the claims 2 and 5 to 15, wherein the fuel cladding tube (11) is produced by a process comprising the steps of: inserting a cylindrical billet of an alloy, which becomes an intermediate layer (15), into another cylindrical billet which becomes an outer surface layer (16) in contact with the reactor water of the

nuclear reactor; inserting into the intermediate layer (15) billet a cylindrical billet which becomes an inner surface layer (14); integrating all of these billets by welding each end face thereof; extruding the integrated billets at a temperature of 500 to 800 °C; and repeating both cold working and annealing thereof by a plurality of times.

19. A method according to claim 16 of producing the structural member for nuclear reactor of any one of claims 3 and 5 to 15, wherein the cylindrical fuel spacer (2) is produced by a process comprising the steps of: inserting a cylindrical billet of an alloy, which becomes an intermediate layer (27), into another cylindrical billet which becomes an outer surface layer (26) in contact with the reactor water of the nuclear reactor; inserting into the intermediate layer (27) billet a cylindrical billet which becomes an inner surface layer and which is made of the same material as the outer surface layer (26); integrating all of the billets by welding each end face thereof; extruding the integrated billets at a temperature not less than 610 °C; and reapeating both cold working and annealing thereof by a plurality of times.

20. A method according to claim 18 or 19, wherein the welding is effected under a pressure not more than 1×10^{-4} Torr.

21. A method according to claim 18 or 19, wherein an intermediate annealing between adjacent two cold workings is effected at a temperature of 610 to 750 °C.

22. A method according to any one of the claims 18 to 21, wherein at least one of both the fuel cladding tube (11) and the cylindrical fuel spacer (2) is subjected to a heat treatment comprising the steps of heating the surface layer of or heating the total thickness of the cladding tube (11) at a temperature of 800 to 900 °C after the final hot working but before the final cold working, and then quenching it.

23. A method according to claim 16 of producing the structural member for nuclear reactor of any one of claims 3 to 15, wherein at least one of the fuel spacer (2) and the fuel channel box (3) is produced by a process comprising the steps of: inserting a plate of an alloy, which becomes an intermediate layer (27), between plate members which become outer surface layers in contact with the reactor water of the nuclear reactor; integrating them by welding each end face thereof; extruding the integrated members at a temperature of 500 to 800 °C; and reapeating both cold working and annealing thereof by a plurality of time.

24. A method according to claim 23, wherein an intermediate annealing between adjacent two cold workings is effected at a temperature of 610 to 750 °C.

25. A method according to claim 23 or 24, wherein at least one of both the fuel spacer (2) and the fuel channel box (3) is subjected to a heat treatment comprising the steps of heating it at a temperature of 800 to 900 °C after the final hot working but before the final cold working with respect to at least one of the fuel cladding tube (11) and cylindrical fuel spacer (2), and then quenching it.

Patentansprüche

1. Strukturteil für eine Brennelementkassette eines Kernreaktors mit einer Dreischichtstruktur, die aufweist:
eine innere Oberflächenschicht, eine äußere Oberflächenschicht und eine dazwischen angeordnete Zwischenschicht, wobei die äußere Oberflächenschicht und gegebenenfalls die innere Oberflächenschicht in Kontakt mit dem Reaktorwasser des Kernreaktors ist bzw. sind,
dadurch **gekennzeichnet**, daß
die äußere Oberflächenschicht und gegebenenfalls die innere Oberflächenschicht aus einer Zirkoniumlegierung besteht bzw. bestehen die Nb, Sn und Mo enthält und dadurch, daß die Zwischenschicht aus einer Legierung mit hoher Verformbarkeit besteht, deren Verformbarkeit größer ist als die der äußeren Oberflächenschicht und deren Festigkeit größer ist als die der inneren Oberflächenschicht.

2. Strukturteil nach Anspruch 1,
dadurch gekennzeichnet, daß
das Teil ein Brennstoffhüllrohr (11) ist und wobei die innere Oberflächenschicht (14) mit dem Kernbrennstoff (21) in Kontakt steht, wobei die innere Oberflächenschicht (14) aus reinem Zirkonium besteht und die Zwischenschicht (15) aus einer hochduktilen Legierung besteht, deren Verformbarkeit

größer ist als die der äußeren Oberflächenschicht (16) und deren Festigkeit größer ist als die der inneren Oberflächenschicht (14).

3. Strukturteil nach Anspruch 1,
dadurch gekennzeichnet, daß
das Teil ein Brennstoffabstandshalter (2) ist.

4. Strukturteil nach Anspruch 1,
dadurch gekennzeichnet, daß
das Teil eine Brennstoff-Channelbox (3) ist.

5. Strukturteil für Kernreaktoren nach einem der Ansprüche 1 bis 4, wobei eine Zirkoniumlegierung mit Nb, Sn und Mo die äußere Oberflächenschicht (16; 26; 31) bildet und gegebenenfalls die innere Oberflächenschicht 0,5 bis 2,2 Gew.% Nb, 0,5 bis 1,5 Gew.% Sn sowie 0,1 bis 0,8 Gew.% Mo aufweist, wobei der Rest aus Zirkonium und nicht vermeidbaren Verunreinigungen besteht.

6. Strukturteil für Kernreaktoren nach einem der Ansprüche 1 bis 5, wobei die hochduktile Legierung, aus der die Zwischenschicht (15; 27) besteht, aus einer Legierung auf Zirkoniumbasis besteht, die Sn, Fe und Ni aufweist.

7. Strukturteil für Kernreaktoren nach Anspruch 6, wobei die Legierung hoher Duktilität aus der die Zwischenschicht (15; 27) besteht aus 0,5 bis 2 Gew.% Sn, 0,05 bis 0,4 Gew.% Fe, 0,03 bis 0,2 Gew.% Ni und dem Rest Zirkonium sowie unvermeidbaren Verunreinigungen besteht.

8. Strukturteil für Kernreaktoren nach einem der Ansprüche 1 bis 5, wobei die hochduktile Legierung, aus der die Zwischenschicht (15; 27) besteht, eine Legierung auf Zirkoniumbasis ist, die Sn, Fe, Ni und Cr aufweist.

9. Strukturelement für Kernreaktoren nach Anspruch 8, bei dem die hochduktile Legierung, aus der die Zwischenschicht (15; 27) besteht 0,5 bis 2 Gew.% Sn, 0,05 bis 0,4 Gew.% Fe, 0,03 bis 0,2 Gew.% Ni, 0,05 bis 0,15 Gew.% Cr, Rest Zirkonium und unvermeidbare Verunreinigungen, aufweist.

10. Strukturelement für Kernreaktor nach einem der Ansprüche 1 bis 5, wobei die hochduktile Legierung, aus der die Zwischenschicht (15; 27) besteht, eine Zirkoniumlegierung ist, die Sn, Fe, Ni, Cr und Mo aufweist.

11. Strukturteil für Kernreaktoren nach Anspruch 10, wobei die hochduktile Legierung, aus der die Zwischenschicht (15; 27) besteht, aus 0,5 bis 2 Gew.% Sn, 0,05 bis 0,4 Gew.% Fe, 0,03 bis 0,2 Gew.% Ni, 0,05 bis 0,15 Gew.% Cr, 0,01 bis 0,8 Gew.% Mo und dem Rest Zirkonium sowie unvermeidbaren Verunreinigungen besteht.

12. Strukturteil für Kernreaktor nach einem der Ansprüche 1 bis 5, wobei die hochduktile Legierung, aus der die Zwischenschicht (15; 27) besteht aus 0,1 bis 0,7 Gew.% Nb, und dem Rest Zirkonium und unvermeidbaren Verunreinigungen besteht.

13. Strukturteil für Kernreaktor nach einem der Ansprüche 1 bis 5, wobei die hochduktile Legierung, aus der die Zwischenschicht (15; 27) besteht, ein rostfreier Stahl ist, der nicht mehr als 0,08 Gew.% C, nicht mehr als 2 Gew.% Mn und nicht mehr als 1 Gew.% Si sowie 16,0 bis 20,0 Gew.% Cr, 8,00 bis 14,00 Gew.% Ni und nicht mehr als 3 Gew.% Mo, Rest Eisen und Verunreinigungen aufweist.

14. Strukturteil für Kernreaktor nach einem der Ansprüche 1 bis 5, wobei die hochduktile Legierung, aus der die Zwischenschicht (15; 27) besteht eine Kupferlegierung ist, die aus nicht mehr als 3 Gew.% Pb, nicht mehr als 6 Gew.% Fe, nicht mehr als 0,5 Gew.% Zn, nicht mehr als 11 Gew.% Al, nicht mehr als 2 Gew.% Mn, nicht mehr als 33 Gew.% Ni sowie dem Rest Kupfer und Verunreinigungen besteht.

15. Strukturteil für Kernreaktor nach einem der Ansprüche 2 und 4 bis 14, wobei bei dem Brennstoffhüllrohr (11) die Dicke der äußeren Oberflächenschicht (16) und gegebenenfalls die Dicke der inneren Oberflächenschicht, die in Kontakt mit dem Reaktorwasser des Kernreaktors steht, 10 bis 30 % der

Gesamtdicke des Hüllrohrs (11) ausmacht bzw. ausmachen und in der Channelbox (3) die Dicke der äußeren Oberflächenschicht (31) in Kontakt mit dem Reaktorwasser 20 bis 35 % der Gesamtdicke der Channelbox ausmacht.

16. Verfahren zur Herstellung eines Strukturteils für eine Brennelementkassette für Kernreaktoren, wobei das Strukturteil eine Dreischichtstruktur aufweist mit:

einer inneren Oberflächenschicht, einer äußeren Oberflächenschicht und einer Zwischenschicht, wobei die äußere Oberflächenschicht und gegebenenfalls die innere Oberflächenschicht in Kontakt mit dem Reaktorwasser des Kernreaktors steht bzw. stehen,

dadurch gekennzeichnet, daß

die äußere Oberflächenschicht und gegebenenfalls die innere Oberflächenschicht aus einer Zirkoniumlegierung besteht bzw. bestehen, die Nb, Sn und Mo aufweist bzw. aufweisen, die Zwischenschicht aus einer hochduktilen Legierung besteht, deren Verformbarkeit größer ist als die der äußeren Oberflächenschicht und die fester ist als die innere Oberflächenschicht, wobei das Verfahren folgende Schritte aufweist: Integration durch thermisches verbinden der dreischichtigen Struktur mit der Zwischenschicht und der inneren und äußeren Oberflächenschichten, wobei die integrierte dreischichtige Struktur einer Wärmebehandlung unterzogen wird, so daß die Struktur aufgeheizt wird, und auf einer Temperatur gehalten wird, in der die α- + β-Phase der Legierung auf Zirkoniumbasis oder die β-Phase der Legierung auf Zirkoniumbasis erhalten werden, und wobei die Struktur nach dem Aufheizen abgeschreckt wird und einer Kaltverformung und einem Ausglühen unterzogen wird, um Teile geringer Dicke zu erzeugen, wobei die verformung und das Verschweißen der dünnen Teile durchgeführt wird, um Strukturteile der gewünschten Form zu erhalten und wobei die Strukturteile einer Wärmebehandlung bei einer Temperatur zwischen 400 und 700 °C unterzogen werden.

17. Verfahren nach Anspruch 16,

dadurch gekennzeichnet, daß

das Teil ein rohrförmiges oder plattenförmiges Teil ist und daß der Schritt der Wärmebehandlung bei einer Temperatur von 400 bis 700 °C ausgeführt wird, nachdem die Endflächen des Teils verschweißt sind.

18. Verfahren nach Anspruch 16 zur Erzeugung des Strukturteils für Kernreaktoren nach einem der Ansprüche 2 und 5 bis 15, wobei das Brennstoffhüllrohr (11) durch ein Verfahren hergestellt wird mit folgenden Schritten: Einführen eines zylinderförmigen Rohlings aus einer Legierung, welcher eine Zwischenschicht (15) wird, in einen anderen zylinderförmigen Rohling, der zur äußeren Oberflächenschicht (16) wird, die in Kontakt mit dem Reaktorwasser des Kernreaktors steht, Einführen eines zylinderförmigen Rohlings, welcher die innere Oberflächenschicht (14) wird, in den Rohling für die Zwischenschicht (15), Zusammenfügen all dieser Rohlinge durch verschweißen ihrer Endflächen und Ziehen der zusammengefügten Rohling bei einer Temperatur von 500 bis 800 °C und mehrmaliges Wiederholen sowohl der Kaltverformung als auch des Glühens.

19. Verfahren nach Anspruch 16 zur Herstellung des Strukturteils für Kernreaktor nach einem der Ansprüche 3 und 5 bis 15, wobei der zylinderförmige Brennstoffabstandshalter (2) durch ein Verfahren hergestellt wird mit folgenden Schritten: Einführen eines zylinderförmigen Rohlings aus einer Legierung, der zu der Zwischenschicht (27) wird, in einen weiteren zylinderförmigen Rohling, der zur äußeren Oberflächenschicht (26) in Kontakt mit dem Reaktorwasser des Kernreaktors wird, Einfügen eines zylinderförmigen Rohlings, der zur inneren Oberflächenschicht wird und der aus demselben Material besteht wie die äußere Oberflächenschicht (26), in den Rohling für die Zwischenschicht (27), Zusammenfügen aller Rohlinge durch Verschweißen der jeweiligen Endflächen, Ziehen der verbundenden Rohlinge bei einer Temperatur von nicht weniger als 610 °C und wiederholtes Kaltverformen und Glühen.

20. Verfahren nach Anspruch 18 und 19, wobei das Verschweißen unter einem Druck nicht größer als 1 x 10^{-4} Torr stattfindet.

21. Verfahren nach Anspruch 18 und 19, wobei das zwischenzeitliche Glühen zwischen aufeinanderfolgenden Kaltverformungen bei einer Temperatur von 610 bis 750 °C stattfindet.

22. Verfahren nach den Ansprüchen 18 bis 21, wobei mindestens ein Teil des Brennstoffhüllrohrs (11) und des zylinderförmigen Brennstoffabstandhalters (2) einer Wärmebehandlung unterzogen wird, die die Schritte aufweist: Aufheizen der Oberflächenschicht oder Aufheizen der Gesamtdicke des Hüllrohrs (11) bei einer Temperatur von 800 bis 900 °C nach der abschließenden Warmverformung, jedoch vor der abschließenden Kaltverformung und anschließendes Abschrecken.

23. Verfahren nach Anspruch 16 zur Herstellung des Strukturteils für Kernreaktoren nach einem der Ansprüche 3 bis 15, wobei mindestens einer des Brennstoffabstandhalters (2) und der Brennstoff-Channelbox (3) durch ein Verfahren hergestellt wird, welches folgende Schritte aufweist: Einfügen einer Platte aus einer Legierung, die zu der Zwischenschicht (27) wird, zwischen Platten, die zur äußeren Oberflächenschicht, die in Kontakt mit dem Reaktorwasser des Kernreaktors ist, wird, Zusammenfügen der Platten durch Verschweißen ihrer Endflächen und Ziehen der zusammengefügten Teile bei einer Temperatur von 500 bis 800 °C sowie wiederholtes Kaltverformen und Glühen.

24. Verfahren nach Anspruch 23, wobei ein Zwischenglühen zwischen zwei aufeinanderfolgenden Kaltverformungen bei einer Temperatur von 610 bis 750 °C durchgeführt wird.

25. Verfahren nach Anspruch 23 und 24, wobei mindestens einer des Brennstoffabstandhalters (2) und der Brennstoff-Channelbox (3) einer Wärmebehandlung unterzogen wird mit folgenden Schritten: Aufheizen auf eine Temperatur von 800 bis 900 °C nach der letzten Warmverformung, jedoch vor der letzten Kaltverformung bezüglich wenigstens entweder dem Brennstoffhüllrohr (11) und dem zylinderförmigen Brennstoffabstandshalter (2) und anschließendes Abschrecken.

Revendications

1. Élément structurel pour un assemblage combustible pour réacteur nucléaire, comprenant une structure à trois couches possédant :
une couche superficielle intérieure, une couche superficielle extérieure et une couche intermédiaire intercalée entre les précédentes, la couche superficielle extérieure et éventuellement la couche superficielle intérieure étant en contact avec l'eau du réacteur nucléaire,
caractérisé en ce que
ladite couche superficielle extérieure et éventuellement la couche superficielle intérieure est/sont réalisées en un alliage à base de Zr contenant Nb, Sn et Mo, et que ladite couche intermédiaire est réalisée en un alliage de haute ductilité, qui possède une ductilité supérieure à celle de la couche superficielle extérieure et qui possède une résistance supérieure à celle de la couche superficielle intérieure.

2. Élément structurel selon la revendication 1, caractérisé en ce que ledit élément est une gaine (11), dans laquelle ladite couche superficielle intérieure (14) est en contact avec le combustible nucléaire (21), laquelle couche superficielle intérieure (14) est réalisée en zirconium pur, et une couche intermédiaire (15) réalisée en un alliage de haute ductilité, qui possède une ductilité supérieure à celle de la couche superficielle extérieure (16) et possède une résistance supérieure à celle de la couche superficielle intérieure (14).

3. Élément structurel selon la revendication 1, caractérisé en ce que ledit élément est un espaceur pour combustible (2).

4. Élément structurel selon la revendication 1, caractérisé en ce que ledit élément est une chemise d'assemblage combustible (3).

5. Élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 1 à 4, dans lequel un alliage à base de Zr contenant Nb, Sn et Mo, lequel alliage forme la couche superficielle extérieure (16; 26; 31), et éventuellement la couche superficielle intérieure, est constitué en poids par 0,5 à 2,2 % de Nb, 0,5 à 1,5 % de Sn, 0,1 à 0,8 % de Mo, le reste étant formé de Zr et d'éventuelles impuretés.

6. Élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 1 à 5, dans lequel l'alliage à haute ductilité constituant la couche intermédiaire (15; 27) est constitué par un alliage

à base de Zr contenant Sn, Fe et Ni.

7. Élément structurel pour réacteur nucléaire selon la revendication 6, dans lequel l'alliage à haute ductilité constituant la couche intermédiaire (15; 27) est constitué en poids, par 0,5 à 2,0 % de Sn, 0,05 à 0,4 % de Fe, 0,03 à 0,2 % de Ni, le reste étant formé de Zr et d'éventuelles impuretés.

8. Élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 1 à 5, dans lequel l'alliage à haute ductilité constituant la couche intermédiaire (15; 27) est un alliage à base de Zr contenant Sn, Fe, Ni et Cr.

9. Élément structurel pour réacteur nucléaire selon la revendication 8, dans lequel l'alliage à haute ductilité constituant la couche intermédiaire (15; 27) est constitué, en poids, par 0,5 à 2,0 % de Sn, 0,05 à 0,4 % de Fe, 0,03 à 0,2 % de Ni, 0,05 à 0,15 % de Cr, le reste étant formé par de Zr et d'éventuelles impuretés.

10. Élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 1 à 5, dans lequel l'alliage à haute ductilité constituant la couche intermédiaire (15; 27) est un alliage à base de Zr contenant Sn, Fe, Ni, Cr et Mo.

11. Élément structurel pour réacteur nucléaire selon la revendication 10, dans lequel l'alliage à haute ductilité constituant la couche intermédiaire (15; 27) est constitué, en poids, par 0,5 à 2,0 % de Sn, 0,05 à 0,4 % de Fe, 0,03 à 0,2 % de Ni, 0,05 à 0,15 % de Cr, 0,01 à 0,8 % de Mo, le reste étant formé de Zr et d'éventuelles impuretés.

12. Élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 1 à 5, dans lequel l'alliage à haute ductilité formant la couche intermédiaire (15; 27) est constitué, en poids, par 0,1 à 0,7 % de Nb, le reste étant formé de Zr et d'éventuelles impuretés.

13. Élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 1 à 5, dans lequel l'alliage à haute ductilité formant la couche intermédiaire (15; 27) est un acier inoxydable constitué, en poids, par pas plus de 0,08 % de C, pas plus de 2,0 % de Mn, pas plus de 1,00 % de Si, 16,0 à 20,0 % de Cr, 8,00 à 14,00 % de Ni, pas plus de 3,00 % de Mo, le reste étant formé de Fe et d'éventuelles impuretés.

14. Élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 1 à 5, dans lequel l'alliage à haute ductilité formant la couche intermédiaire (15; 27) est un alliage à base de Cu constitué, en poids, par pas plus de 3,0 % de Pb, pas plus de 6,0 % de Fe, pas plus de 0,5 % de Zn, pas plus de 11,0 % de Al, pas plus de 2,0 % de Mn, pas plus de 33,0 % de Ni, le reste étant formé de Cu et d'éventuelles impuretés.

15. Élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 2 et 4 à 14, dans lequel, dans la gaine (11), l'épaisseur de la couche superficielle extérieure (16) et éventuellement de la couche superficielle intérieure en contact avec l'eau du réacteur nucléaire est comprise entre 10 et 30 % de l'épaisseur totale de la gaine (11), et, dans la chemise (3), l'épaisseur de la couche superficielle extérieure (31) en contact avec elle est comprise entre 20 et 35 % de l'épaisseur totale de la chemise.

16. Élément structurel pour un assemblage combustible pour réacteur nucléaire, ledit élément structurel comprenant une structure à trois couches comprenant :
une couche superficielle intérieure, une couche superficielle extérieure et une couche intermédiaire, ladite couche superficielle extérieure et éventuellement ladite couche superficielle intérieure étant en contact avec l'eau du réacteur nucléaire,
caractérisé en ce que
ladite couche superficielle extérieure et éventuellement la couche superficielle intérieure est/sont réalisées en un alliage à base de Zr contenant Nb, Sn et Mo,
ladite couche intermédiaire est réalisée en un alliage à haute ductilité, qui possède une ductilité supérieure à la couche superficielle extérieure et qui possède une résistance supérieure à celle de la surface de la couche superficielle intérieure,
ledit procédé comprend les étapes consistant à : intégrer, grâce à l'utilisation d'une liaison thermique,

ladite structure a trois couches comprenant ladite couche intermédiaire et lesdites couches superficielles intérieure et extérieure en soumettant ladite structure intégrée à trois couches à un traitement thermique de sorte que ladite structure est chauffée et maintenue à une température de la phase α + β dudit alliage à base de Zr ou de la phase β dudit alliage à base de Zr et de telle sorte que ladite structure est refroidie brusquement après le chauffage; soumettre la structure à trois couches ayant subi le traitement thermique à une déformation plastique à froid et à un recuit pour obtenir ainsi un élément de faible épaisseur; appliquer un travail de déformation et de soudage à l'élément de faible épaisseur pour obtenir l'élément structurel possédant une forme désirée; et soumettre l'élément structurel à un traitement thermique à une température de 400 à 700 °C.

17. Procédé selon la revendication 16, caractérisé en ce que ledit élément est un élément tubulaire ou en forme de plaque et l'étape d'exécution d'un traitement thermique à une température de l'ordre de 400 à 700 °C est exécutée après le soudage de la face d'extrémité dudit élément.

18. Procédé selon la revendication 16 pour fabriquer l'élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 2 et 5 à 15, selon lequel on fabrique la gaine (11) à l'aide d'un procédé comprenant les étapes consistant à : insérer une billette cylindrique d'un alliage, qui devient une couche intermédiaire (15), dans une autre billette cylindrique qui devient une couche superficielle extérieure (16) en contact avec l'eau du réacteur nucléaire; insérer, dans la billette de la couche intermédiaire (15), une billette cylindrique qui devient une couche superficielle intérieure (14); intégrer toutes ces billettes par soudage de chaque face d'extrémité de ces billettes; extruder les billettes intégrées à une température de 500 à 800 °C; et répéter plusieurs fois la déformation à froid et le recuit de ces billettes.

19. Procédé selon la revendication 16 pour fabriquer l'élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 3 et 5 à 15, selon lequel on fabrique l'espaceur cylindrique (2) au moyen d'un procédé comprenant les étapes consistant à : insérer une billette cylindrique d'un alliage, qui devient une couche intermédiaire (27), dans une autre billette cylindrique qui devient une couche superficielle extérieure (26) en contact avec l'eau du réacteur nucléaire; insérer, dans la billette de la couche intermédiaire (27), une billette cylindrique qui devient une couche superficielle intérieure et qui est réalisée avec le même matériau que la couche superficielle extérieure (26); intégrer toutes les billettes par soudage de chaque face d'extrémité de ces billettes; extruder les billettes intégrées à une température non inférieure à 610 °C; et répéter à plusieurs fois la déformation à froid et le recuit des billettes.

20. Procédé selon la revendication 18 ou 19, selon lequel le soudage est exécuté à une pression non supérieure à 1×10^{-4} torr.

21. Procédé selon la revendication 18 ou 19, selon lequel un recuit intermédiaire entre deux déformations à froid successives est exécuté à une température de 610 à 750 °C.

22. Procédé selon l'une quelconque des revendications 18 à 21, selon lequel on soumet la gaine (11) et/ou l'espaceur cylindrique (2) à un traitement thermique comprenant les étapes consistant à chauffer la couche superficielle ou à chauffer, sur toute son épaisseur, la gaine (11) à une température comprise entre 800 et 900 °C après la déformation finale à chaud, mais avant la déformation finale à froid, puis à lui appliquer un refroidissement brusque.

23. Procédé selon la revendication 16 pour fabriquer l'élément structurel pour réacteur nucléaire selon l'une quelconque des revendications 3 à 15, selon lequel on fabrique l'espaceur (2) et/ou la chemise (3) au moyen d'un procédé comprenant les étapes consistant à : insérer une plaque formée d'un alliage, qui devient une couche intermédiaire (27), entre des éléments en forme de plaques qui deviennent les couches superficielles extérieures en contact avec l'eau du réacteur nucléaire; intégrer ces éléments par soudage de chacune des faces d'extrémité de ces éléments; extruder les éléments intégrés à une température de 500 à 800 °C; et répéter plusieurs fois la déformation à froid et le recuit de ces éléments.

24. Procédé selon la revendication 23, selon lequel un recuit intermédiaire entre deux déformations à froid successives est exécuté à une température de 610 à 750 °C.

25. Procédé selon la revendication 23 ou 24, selon lequel on soumet l'espaceur (2) et/ou la chemise (3) à un traitement thermique comprenant les étapes consistant à chauffer l'espaceur et/ou la chemise à une température de 800 °C après la déformation finale à chaud, mais avant la déformation finale à froid en rapport avec la gaine (11) et/ou l'espaceur cylindrique (2), puis à lui appliquer refroidissement brusque.

FIG. 1A

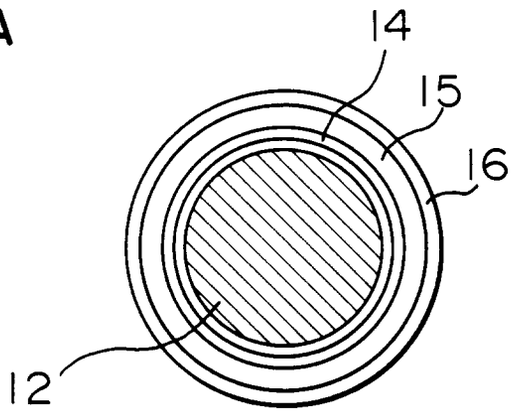


FIG. 1B

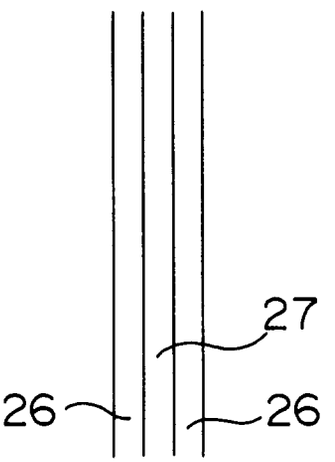


FIG. 1C

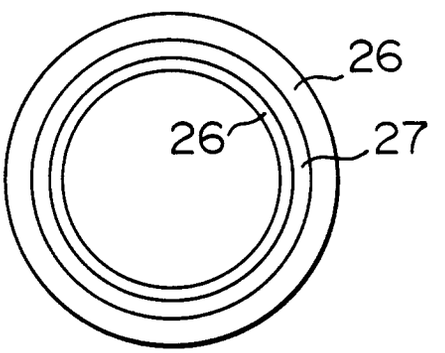


FIG. 2

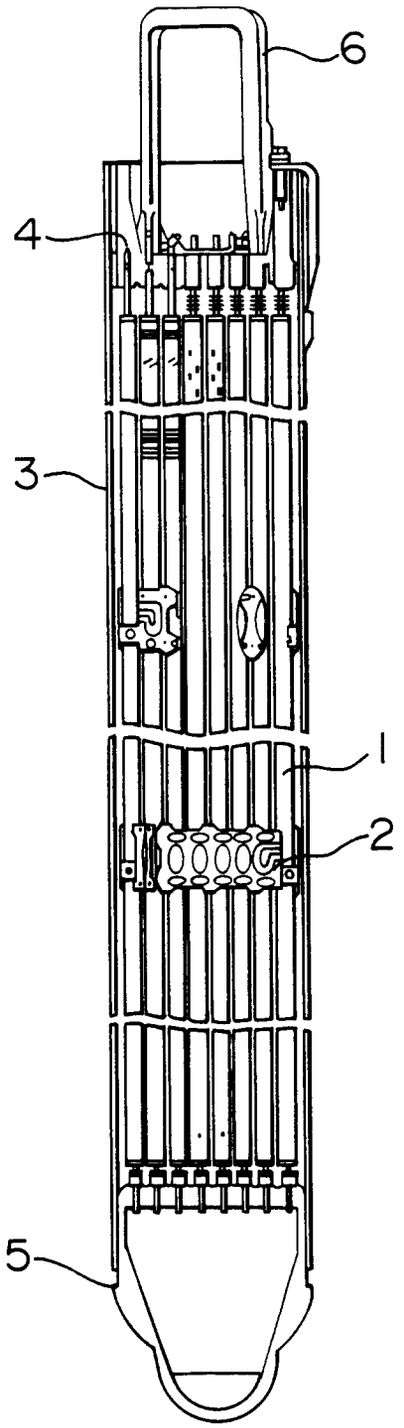


FIG. 3

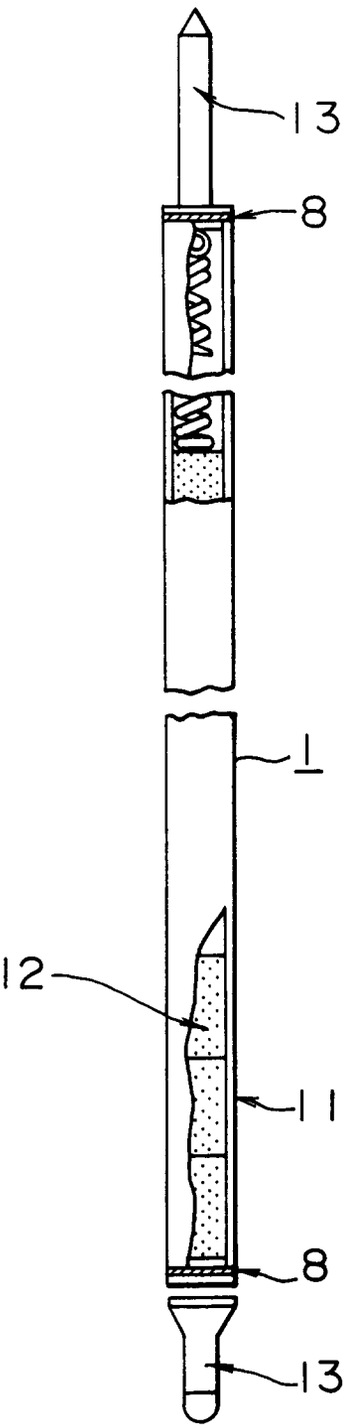


FIG. 4A

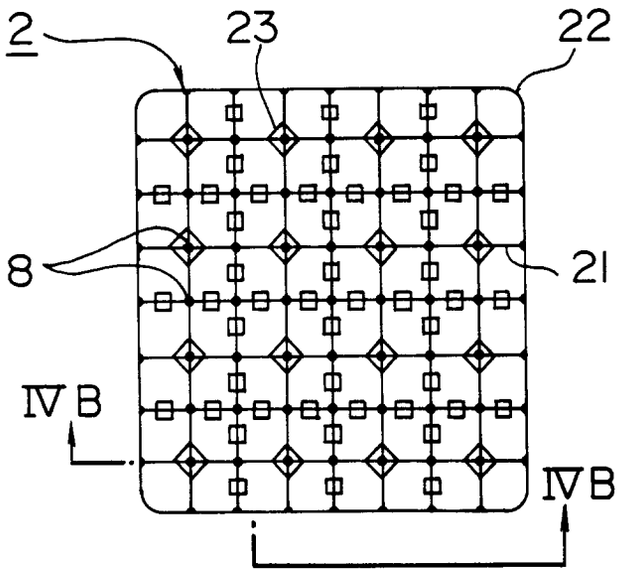


FIG. 4B

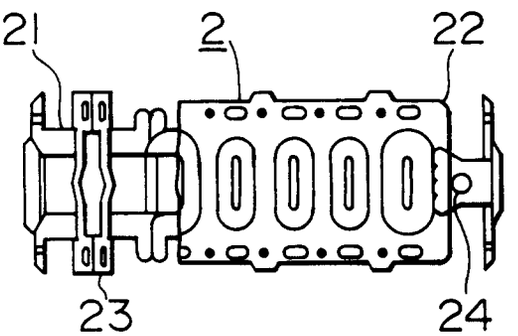


FIG. 4C

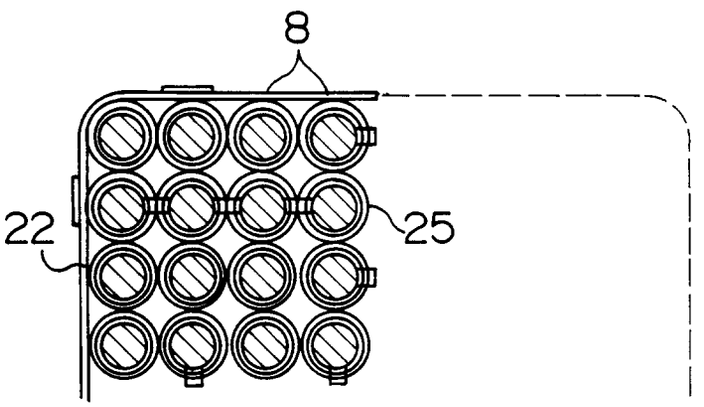


FIG. 4D

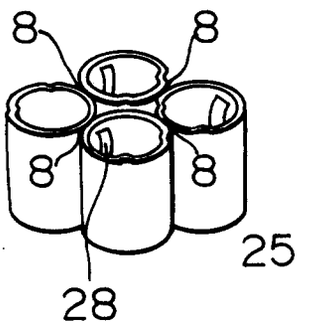


FIG. 5

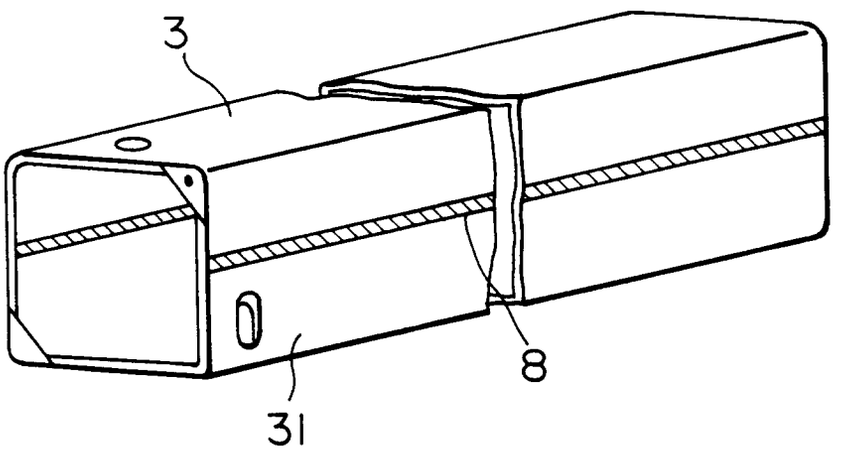


FIG. 6

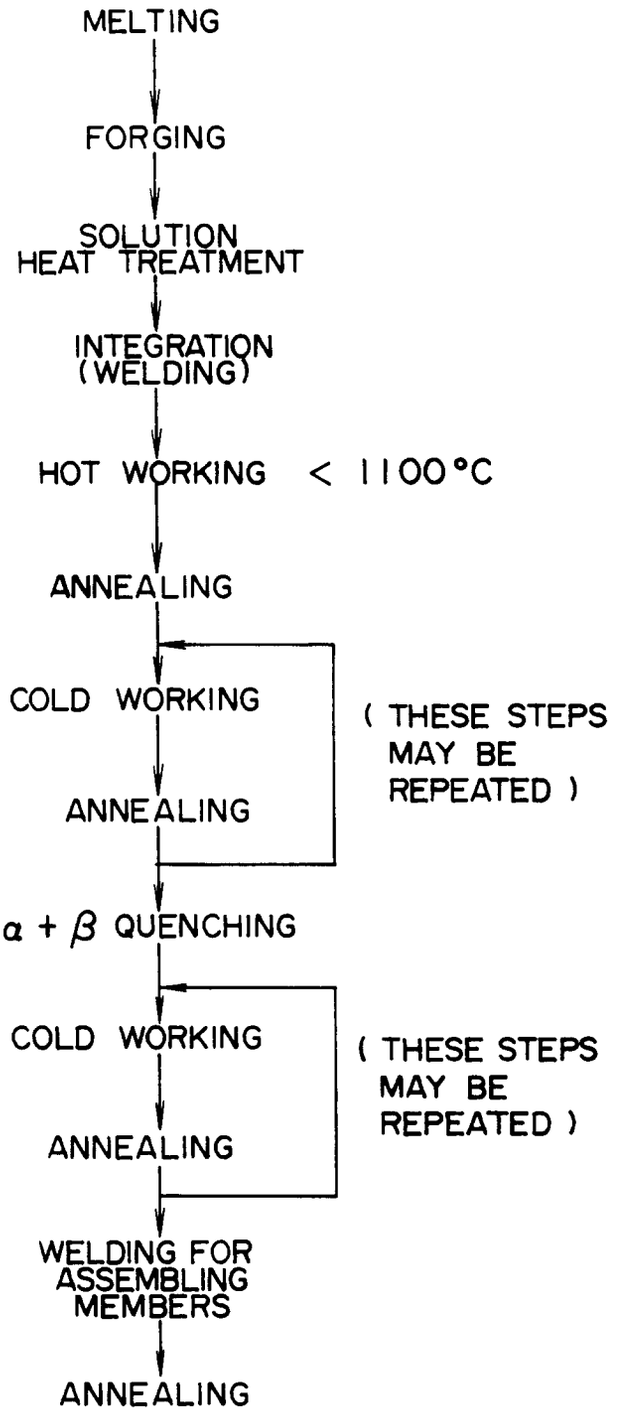

MELTING
FORGING
SOLUTION HEAT TREATMENT
INTEGRATION (WELDING)
HOT WORKING < 1100°C
ANNEALING
COLD WORKING
ANNEALING
(THESE STEPS MAY BE REPEATED)
α + β QUENCHING
COLD WORKING
ANNEALING
(THESE STEPS MAY BE REPEATED)
WELDING FOR ASSEMBLING MEMBERS
ANNEALING

FIG. 7

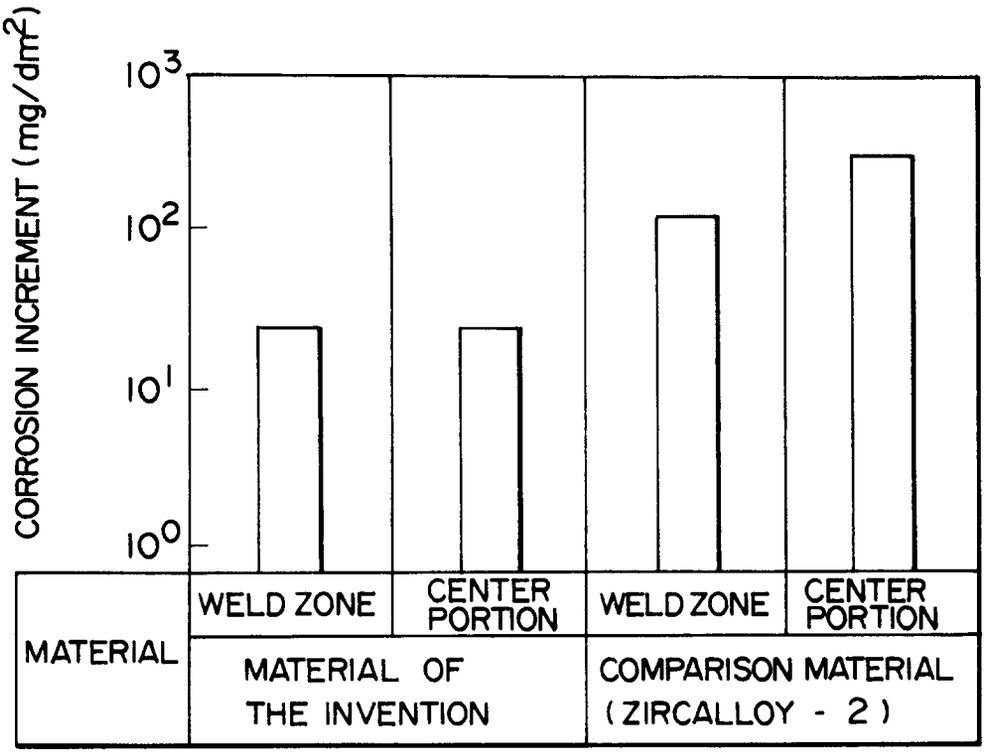
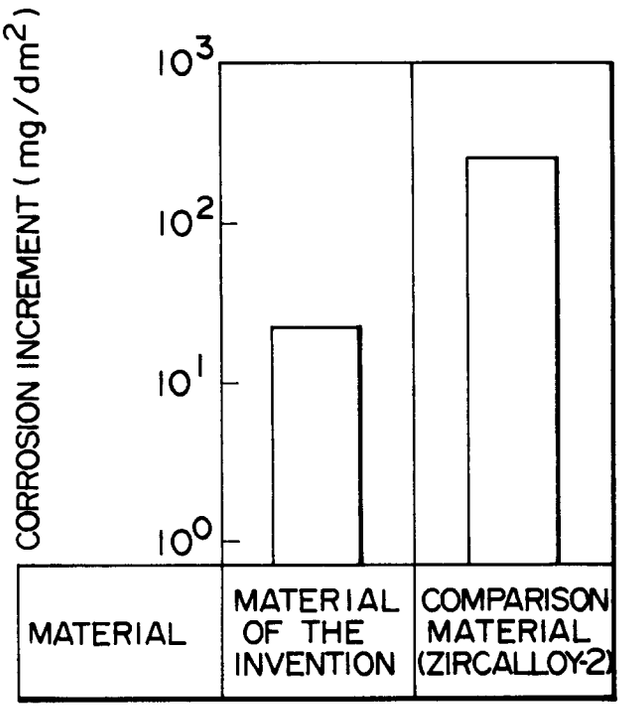

CORROSION INCREMENT (mg/dm²)
10³
10²
10¹
10⁰
WELD ZONE
CENTER PORTION
WELD ZONE
CENTER PORTION
MATERIAL
MATERIAL OF THE INVENTION
COMPARISON MATERIAL (ZIRCALLOY - 2)

FIG. 8


CORROSION INCREMENT (mg/dm²)
10³
10²
10¹
10⁰
MATERIAL
MATERIAL OF THE INVENTION
COMPARISON MATERIAL (ZIRCALLOY-2)